Oct. 10, 1972 W. J. TIMSON 3,697,270

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Dec. 21, 1970 6 Sheets-Sheet 1

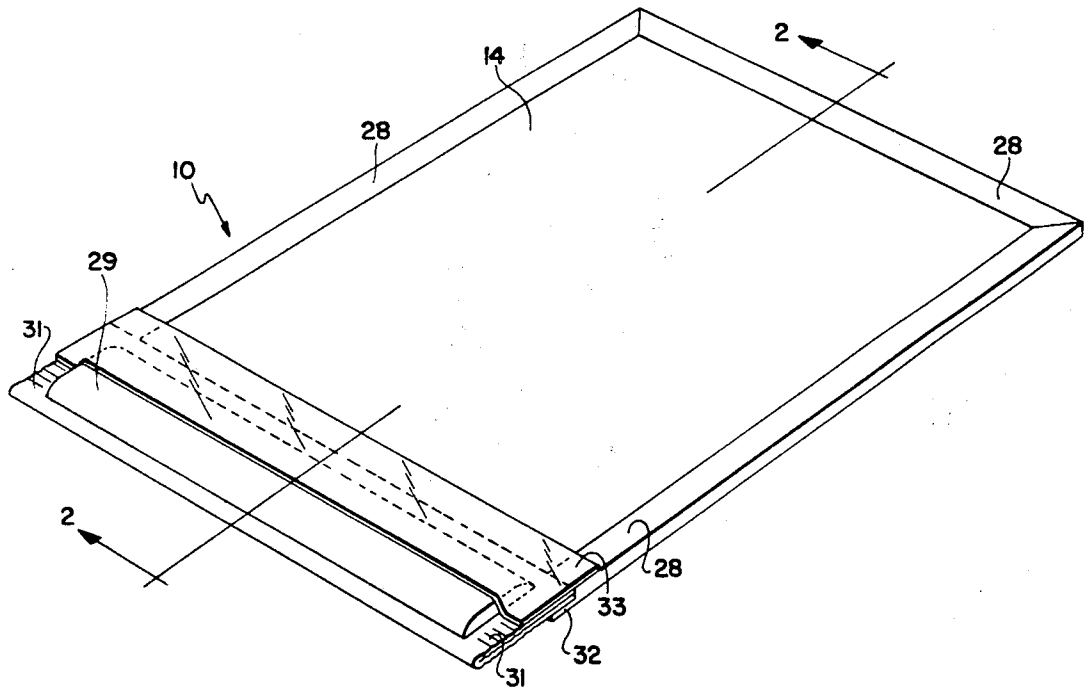


FIG. 1

INVENTOR.
WILLIAM J. TIMSON

BY
Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

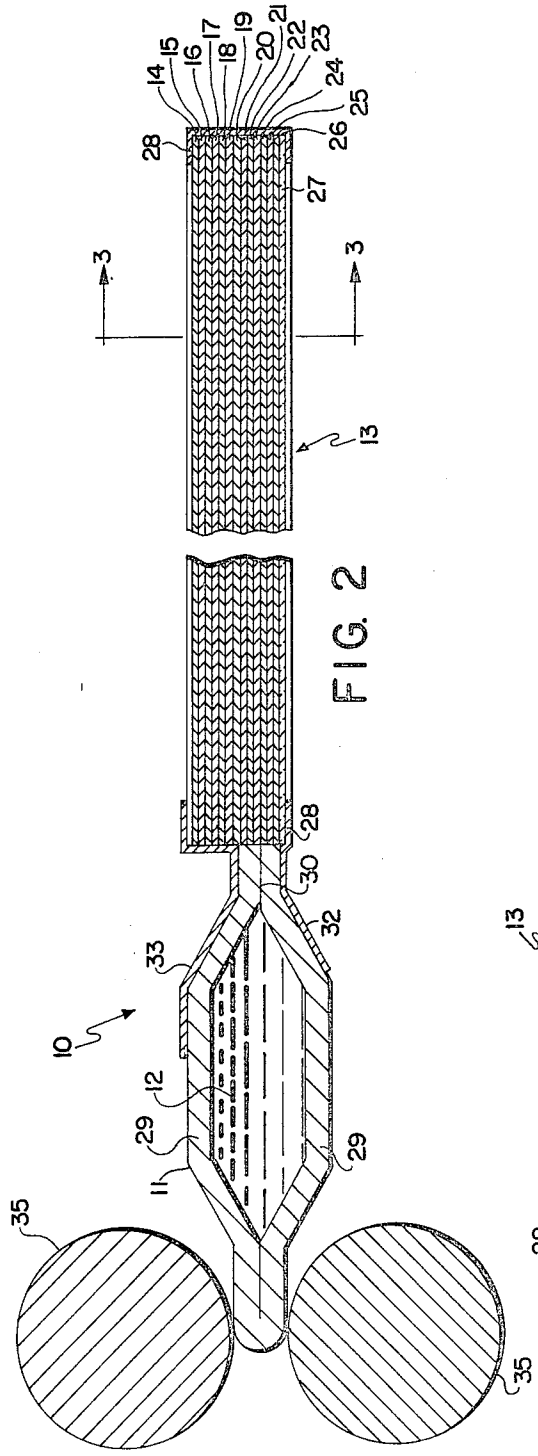


FIG. 2

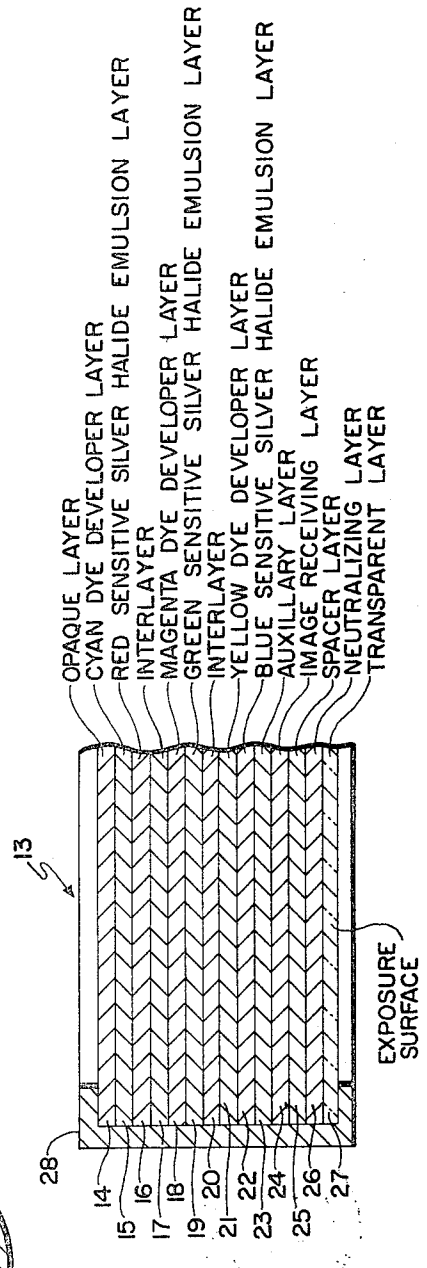


FIG. 3

INVENTOR.
WILLIAM J. TIMSON

BY

Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Dec. 21, 1970 6 Sheets-Sheet 3

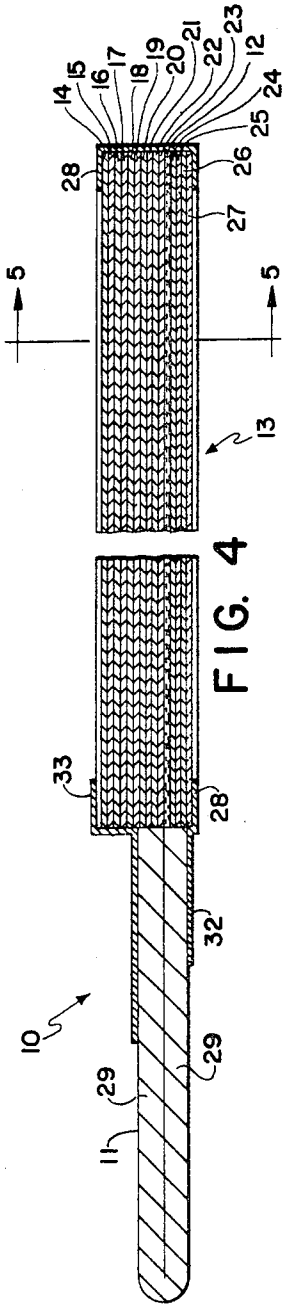


FIG. 4

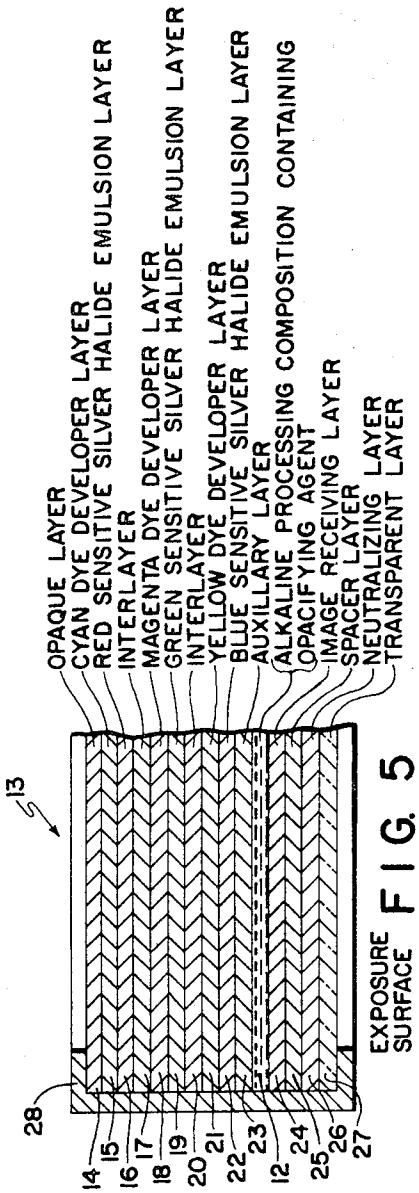


FIG. 5

INVENTOR.
WILLIAM J. TIMSON

BY

Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

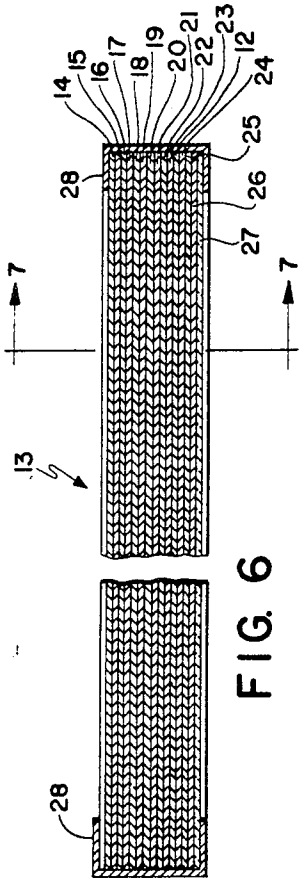


FIG. 6

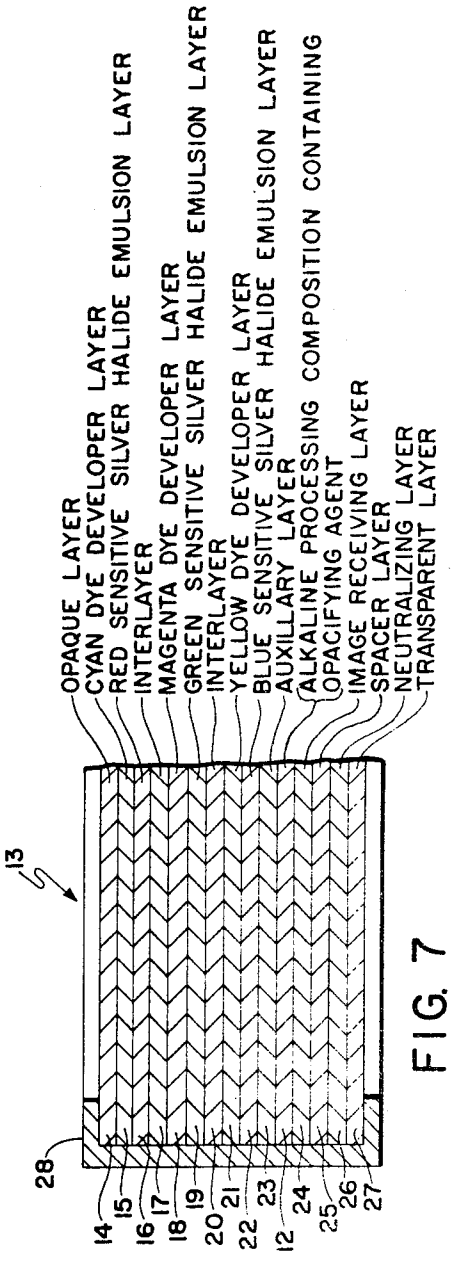


FIG. 7

INVENTOR.
WILLIAM J. TIMSON

BY

Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

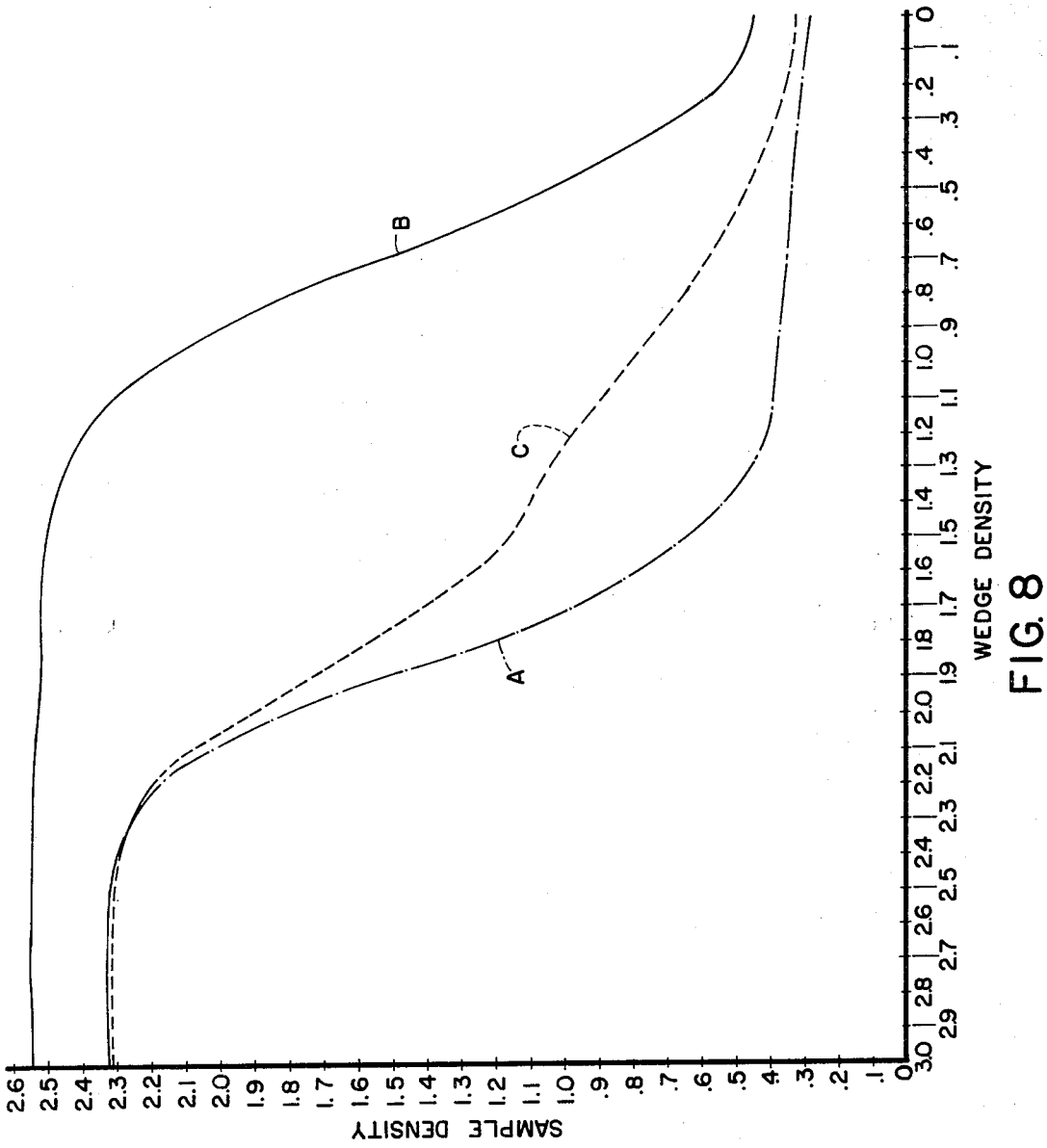


FIG. 8

INVENTOR.
WILLIAM J. TIMSON

BY

Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Dec. 21, 1970 6 Sheets-Sheet 6

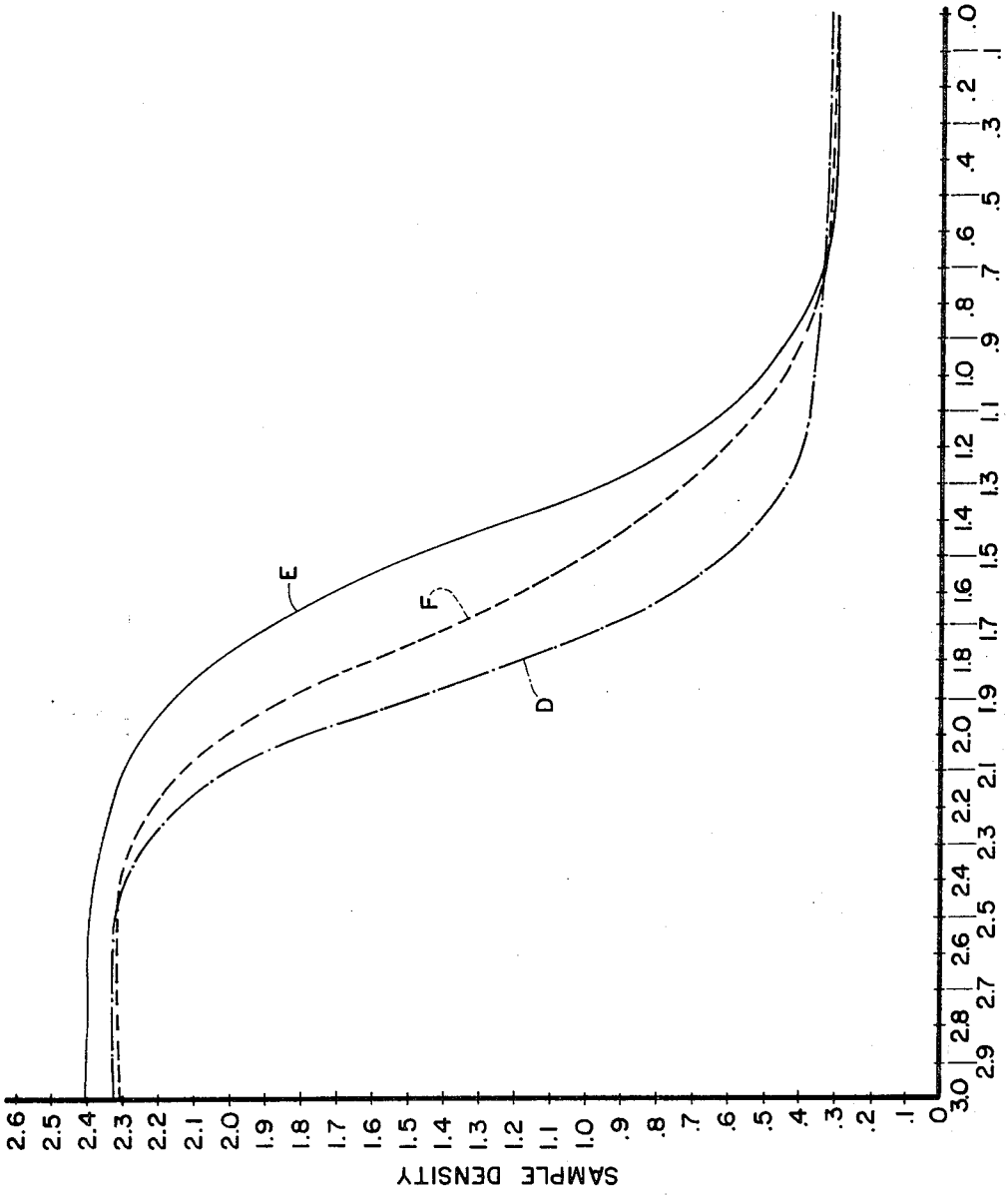


FIG. 9

INVENTOR.
WILLIAM J. TIMSON

BY

Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

United States Patent Office 3,697,270
Patented Oct. 10, 1972

3,697,270

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

William J. Timson, Belmont, Mass., assignor to Polaroid Corporation, Cambridge, Mass.

Filed Dec. 21, 1970, Ser. No. 99,971
Int. Cl. G03c 1/40, 1/48, 5/54
U.S. Cl. 96—3 29 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to photography and, more particularly, to diffusion transfer process photographic film units which comprise a photosensitive element adapted to provide, by diffusion transfer photographic processing, selective dye image recordation of incident actinic radiation as a function of the point-to-point degree of photosensitive element exposure, which film unit includes a plurality of essential layers including a direct negative photosensitive silver halide layer having associated therewith dye image-forming material which is diffusible during processing as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation and comprising a plurality of photosensitive silver halide dispersions which comprise silver halide grains, the majority of which possess a substantially uniform grain size and which dispersions taken together possess a mean particle size within the range of ~0.5 to 3.0μ and a layer adapted to receive image-forming material diffusing thereto; and to specified diffusion transfer processes employing such film units.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention is directed to providing new and improved diffusion transfer process photographic film units adapted to provide, as a function of the point-to-point degree of photoexposure, by diffusion transfer processing a dye transfer image.

(2) Description of prior art

As disclosed in U.S. Pat. No. 3,415,644, a composite photosensitive structure, particularly adapted for reflection type photographic diffusion transfer color process employment, which comprises a plurality of essential layers including, in sequence, a dimensionally stable opaque layer; one or more silver halide emulsion layers having associated therewith dye image-providing material which is soluble and diffusible, in alkali, at a first pH, as a function of the point-to-point degree of its associated silver halide emulsion's exposure to incident actinic radiation; a polymeric layer adapted to receive solubilized dye image-providing material diffusing thereto; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition from the first pH to a second pH at which the dye image-providing material is substantially nondiffusible; and a dimensionally stable transparent layer, may be exposed to incident actinic radiation and processed by interposing, intermediate the silver halide emulsion layer and the reception layer, an alkaline processing composition processing the first pH and containing opacifying agent, which may reflect incident radiation, in a quantity sufficient to mask dye image-providing material associated with the silver halide emulsion.

In a preferred embodiment, the composite photosensitive structure includes a rupturable container, retaining the alkaline processing composition having the first pH and opacifying agent, fixedly positioned extending transverse a leading edge of the composite structure in order to effect, upon application of compressive pressure to the container, discharge of the processing composition intermediate the opposed surfaces of the reception layer and the next adjacent silver halide emulsion.

The liquid processing composition, distributed intermediate the reception layer and the silver halide emulsion, permeates the silver halide emulsion layers of the composite photosensitive structure to initiate development of the latent images contained therein resultant from photoexposure. As a consequence of the development of the latent images, dye image-providing material associated with each of the respective silver halide emulsion layers is individually mobilized as a function of the point-to-point degree of the respective silver halide emulsion layer's photoexposure, resulting in imagewise distributions of mobile dye image-providing materials adapted to transfer, by diffusion, to the reception layer to provide the desired transfer dye image. Subsequent to substantial dye image formation in the reception layer, a sufficient portion of the ions of the alkaline processing composition transfers, by diffusion, to the polymeric neutralizing layer to effect reduction in the alkalinity of the composite film unit to the second pH at which dye image-providing material is substantially nondiffusible, and further dye image-providing material transfer is thereby substantially obviated.

The transfer dye image is viewed, as a reflection image, through the dimensionally stable transparent layer against the background provided by the opacifying agent, distributed as a component of the processing composition, intermediate the reception layer and next adjacent silver halide emulsion layer. The thus-formed opacifying stratum effectively masks residual dye image-providing material retained in association with the silver halide emulsion layer subsequent to processing.

In U.S. Pat. No. 3,415,646, the dimensionally stable layer of the film unit next adjacent the photosensitive silver halide layer or layers is disclosed to be transparent to incident actinic radiation and as disclosed in U.S. Pat. No. 3,415,645, in such instance the opacifying agent may be initially disposed in the film unit intermediate the reception layer and next adjacent silver halide layer.

As disclosed in the copending U.S. patent application Ser. No. 846,441 of Edwin H. Land, filed July 31, 1969 now U. S. Pat. No. 3,615,421 issued Oct. 26, 1971 and the copending U.S. patent application Ser. No. 3,646 now abandoned, of Sheldon A. Buckler, filed Jan. 19, 1970, the opacifying component of the film unit may optionally be initially disposed as a preformed processing composition permeable layer, intermediate the reception layer and next adjacent silver halide layer, in a concentration which prior to photoexposure is insufficient to prevent transmission therethrough of exposing actinic radiation and which, subsequent to processing, possesses an opacifying capacity effective to mask residual dye image-providing material retained associated with the film unit's silver halide emulsion layers, and in the copending U.S. patent application Ser. No. 43,742 of Edwin H. Land, filed June 5, 1970, now U.S. Pat. 3,647,435

the opacifying component of the film unit may optionally be initially formed in situ, intermediate the reception layer and next adjacent silver halide layer, during photographic processing of the film unit.

In the copending U.S. patent applications of Edwin H. Land, Ser. No. 786,352, filed Dec. 23, 1968, and Ser. No. 43,782, filed June 5, 1970, the opacifying component is disclosed to optionally comprise a light-absorbing reagent such as a dye which is present as an absorbing species at the first pH and which may be converted to a substantially non-absorbing species at the second pH, and in U.S. Pat. No. 3,473,925 and the copending U.S. patent applications of Terry W. Milligan and Richard W. Young, Ser. No. 846,177, filed July 30, 1969, now U.S. Pat. No. 3,573,042 issued Mar. 30, 1971, and Ser. No. 864,397, filed Oct. 7, 1969 now U.S. Pat. No. 3,576,626 issued Apr. 27, 1971, opacifying and reflecting component, respectively, may be individually interposed intermediate the silver halide layer and reception layer by selective distribution from a composite or a plurality of rupturable containers.

In the copending U.S. patent application Ser. No. 782,056 of Edwin H. Land, filed Dec. 9, 1968 now U.S. Pat. No. 3,573,043 issued Mar. 30, 1971, the polymeric neutralizing layer is disclosed to be optionally disposed intermediate the dimensionally stable opaque layer and next adjacent essential layer, i.e., next adjacent silver halide/dye image-providing material component, to effect the designated modulation of film unit's environmental pH; the copending U.S. patent application Ser. No. 846,442 of Edwin H. Land, filed July 31, 1969 now U.S. Pat. No. 3,576,625 issued Apr. 27, 1971, discloses the employment of particulate acid distributed within the film unit to effect the modulation of the environmental pH, and the copending U.S. patent application Ser. No. 782,075 of Edwin H. Land, filed Dec. 9, 1968 now U.S. Pat. No. 3,573,044 issued Mar. 30, 1971, discloses the employment of processing composition solvent vapor transmissive dimensionally stable layers to effect process modulation of dye transfer as a function of solvent concentration.

Where desired, the film unit may also be constructed in accordance with the disclosure of the copending U.S. patent applications of Howard G. Rogers, Ser. No. 39,646, filed May 22, 1970 now U.S. Pat. No. 3,594,165 issued July 20, 1971, and Ser. No. 39,666, filed May 22, 1970 now U.S. Pat. No. 3,594,164 issued July 20, 1971, to comprise a composite photosensitive structure including a transparent dimensionally stable layer carrying a reception layer, a processing composition permeable opaque layer and a photosensitive silver halide layer and the film unit may include a separate dimensionally stable sheet element adapted to be superposed on the surface of the photosensitive structure opposite the dimensionally stable layer and may further include a rupturable container retaining processing composition and adapted to distribute the composition intermediate the sheet and photosensitive structure to effect processing. As further disclosed in the last-cited applications, in structures wherein the receptor is positioned next adjacent the transparent layer or the processing composition and/or the sheet is to be separated from the remainder of the film unit subsequent to processing, the latter elements may optionally include opacifying component.

As disclosed in copending U.S. patent application Ser. No. 3645 of Edwin H. Land, filed Jan. 19, 1971 now U.S. Pat. No. 3,620,724 issued Nov. 16, 1971 and the copending U.S. patent application Ser. No. 3691 of Sheldon A. Buckler, filed Jan. 19, 1970, now abandoned, the dimensionally stable layer referred to may be opaque and in which instance the photosensitive silver halide layer is positioned next adjacent the opaque support layer and the opacifying component of the film unit's processing composition permeable opaque layer will be disposed in the unit in a concentration insufficient to prevent transmission therethrough of exposing actinic radiation and which, subsequent to processing, possesses an opacifying capacity effective to mask residual dye image-providing material retained associated with the silver halide layer, and as disclosed in the copending U.S. patent application Ser. No. 43,741 of Edwin H. Land, filed June 5, 1970, now U.S. Pat. 3,647,434 the opacifying agent may be optionally formed in such film unit, in situ, during processing of the unit.

SUMMARY OF THE INVENTION

The present invention is directed to a new and improved, preferably integral negative/positive, diffusion transfer process photographic film unit adapted to provide, by diffusion transfer processing, photographic color image reproduction as a function of exposure of such film unit to incident actinic radiation.

The film unit assemblage construction to be employed in the practice of the present invention preferably comprises a film unit of the general type set forth in aforementioned U.S. Pats. Nos. 3,415,644, -5 and -6 and 3,473,925 and copending U.S. patent applications Ser. Nos. 782,056 now U.S. Pat. No. 3,573,043; 782,075 now U.S. Pat. No. 3,573,044; 786,352; 846,177 now U.S. Pat. No. 3,573,042; 846,441 now U.S. Pat. No. 3,615,421; 846,442 now U.S. Pat. No. 3,576,625; 864,397 now U.S. Pat. No. 3,576,626; 3645 now U.S. Pat. No. 3,620,724; 3691, now abandoned; 39,646 now U.S. Pat. No. 3,594,165; 39,666 now U.S. Pat. No. 3,594,164; 43,741, now U.S. Pat. No. 3,647,434; 43,742; and 43,782 and in U.S. Pat. Nos. 2,983,606 and 3,345,163; and will include a photosensitive silver halide layer which comprises a plurality of photosensitive silver halide dispersions, in intimate admixture, which comprise silver halide grains the majority of which possess a substantially uniform grain size and which dispersions taken together possess a mean particle size within the range of ~0.5 to 3.0μ disposed in a photosensitive element which contains a plurality of layers including, in relative order, a dimensionally stable layer preferably opaque to incident actinic radiation; one or more photosensitive silver halide layers having associated therewith dye image-forming material which is processing composition diffusible as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive image-forming material diffusing thereto; a dimensionally stable layer transparent to incident actinic radiation; and means for interposing, intermediate the silver halide layers and the reception layer, opacifying agent and a processing composition, and, in a particularly preferred embodiment, a processing composition possessing a first pH at which the dye image-forming material is diffusible during processing and means for modulating the pH of the film unit from the first pH to a second pH at which the dye image-forming material is substantially nondiffusible subsequent to substantial dye transfer image formation.

In accordance with a specifically preferred embodiment of the present invention, a film unit assemblage of the aforementioned general structural parameters will be adapted to be processed, subsequent to photoexposure, in the presence of actinic radiation and may be fabricated to employ, as means interposed intermediate the reception layer and next adjacent silver halide layer subsequent to photoexposure, an inorganic light-reflecting pigment dispersion containing reflecting pigment and at least one optical filter agent, at a pH above the pKa of the optical filter agent and at which pH the dye image-forming material is diffusible during processing as a function of silver halide layer photoexposure, in a concentration in admixture effective to provide a barrier to transmission of actinic radiation therethrough, and the means for interposing the opacifying agent and the processing composition, a rupturable container, retaining the opacifying agent disposed in the processing composition selected, fixedly positioned extending transverse a leading edge of the film

unit and adapted, upon application of compressive pressure, to distribute its contents intermediate the reception layer and next adjacent silver halide layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a photographic film unit embodying the invention;

FIGS. 2, 4 and 6 are diagrammatic enlarged cross-sectional views of the film unit of FIG. 1, along section line 2—2, illustrating the association of elements during the three illustrated stages of the performance of a diffusion transfer process, for the production of a multicolor transfer image according to the invention, the thickness of the various materials being exaggerated, and wherein FIG. 2 represents an exposure stage, FIG. 4 represents a processing stage and FIG. 6 represents a product of the process;

FIGS. 3, 5 and 7 are diagrammatic, further enlarged cross-sectional views of the film unit of FIGS. 2, 4 and 6, along section lines 3—3, 5—5 and 7—7, respectively, further illustrating, in detail, the arrangement of layers comprising the photosensitive laminate during the three illustrated stages of the transfer process; and

FIGS. 8 and 9 are graphic representations of the characteristic curves of monochromatic dye transfer images of the present invention compared with control transfer images.

DETAILED DESCRIPTION OF THE INVENTION

As previously characterized, diffusion transfer photographic processing may be employed to provide a positive reflection dye image, as a direct function of actinic radiation incident on a film unit assemblage which unit is preferably constructed to comprise a plurality of sequential layers including a dimensionally stable layer most preferably opaque to incident radiation; a photosensitive silver halide layer having associated therewith dye image-forming material which is processing composition diffusible at a selected first pH as a function of the point-to-point degree of silver halide layer photoexposure; a layer adapted to receive dye image-forming material diffusing thereto; a dimensionally stable layer transparent to incident radiation; means for interposing, intermediate the silver halide layer and the reception layer, opacifying agent and preferably an inorganic reflecting pigment dispersion containing at least one optical filter agent or dye in a concentration effective to provide, subsequent to selective photoexposure of the silver halide layer, protection of the silver halide layer from further exposure to actinic radiation incident on the dimensionally stable layer; means for converting the pH of the film unit from the first pH to a second pH at which the dye image-forming material is substantially nondiffusible subsequent to substantial dye image-forming material diffusion to the reception layer; and wherein the dimensionally stable layers, taken together, possess a processing composition solvent vapor permeability adapted to effect, subsequent to substantial dye transfer image formation and preceding substantial dye transfer image degradation, osmotic transpiration of processing composition solvent in a quantity effective to decrease a first solvent concentration at which the dye image-forming material is soluble and diffusible as a function of processing to a second solvent concentration at which the dye image-forming material is substantially nondiffusible.

It now has been discovered, however, that improved photographic reproduction in color by diffusion transfer processing may be accomplished by employment of a diffusion transfer process film unit which comprises a plurality of layers including photosensitive layer comprising photosensitive silver halide grains the majority of which possess a substantially uniform grain size within the range of $\sim$0.5 to 3.0μ having associated therewith a dye image-providing material which is diffusible, during processing of the unit, as a function of the point-to-point degree of the photosensitive layer's exposure to incident actinic radiation, and a layer adapted to receive dye image-providing material diffusing thereto.

In the preferred embodiment of the present invention, $>\sim$75% and most preferably $>\sim$90% of the photosensitive silver halide grains constituting the photosensitive layer possess a substantially uniform grain size distribution, preferably within $\pm\sim$10%, by weight, of the selected grain size.

Employment of diffusion transfer color process film units possessing photosensitive silver halide components exhibiting the restricted grain size distribution described has been discovered to provide markedly increased diffusion transfer processing temperature latitude; film unit storage stability; and more efficient and effective utilization of silver, dye image-providing components and photographic adjuvants as, for example, sensitizing dye components of the film unit. Specifically, the employment of the silver halide grain size distribution denoted specifically facilitates the avoidance of the presence as a component of the photosensitive silver halide layer of a substantial proportion or number of grains possessing a diameter $>\sim$3.0μ which grains possess, as a function of surface area, a proclivity for formation of undesired fog, which proclivity increases as a direct function of increase in processing temperature, with the concomitant results of less efficient and effective utilization of a selected silver halide concentration per unit weight, degradation of image recordation acuity and corresponding dye transfer image construction. Conversely, the presence of a substantial number of grains possessing a diameter $<\sim$0.5μ is also avoided, such grains having been found to exhibit relatively low effective sensitivity to exposure radiation, thus also resultant in less efficient utilization of silver halide to provide dye transfer image formation as a function of the film unit's exposure to actinic radiation.

Recognizing that although efficient utilization of silver halide in terms of its active species film unit coverage requirement decreases the excess quantities of silver halide, dye image-providing material and photographic adjuvants necessary to factor out inefficient silver halide grain performance, most importantly control of the image-wise generation of and transfer of dye image-providing material is most accurately accomplished employing a silver halide grain distribution the sum total grains of which are active to individually contribute to selective generation and transfer of the image-providing components.

In accordance with the present invention, it has been discovered that excellent diffusion transfer dye image characteristic curve shape control, i.e., control of the transfer image characteristics represented graphically by the curve integrating dye density of the transfer image as a function of the log exposure of the photosensitive silver halide layer, may be obtained by utilization of a photosensitive silver halide layer which comprises a blend of differentially photosensitive silver halide dispersion each possessing a substantially uniform grain size distribution wherein the dispersions in admixture possess a mean particle size within the previously denoted range of $\sim$0.5 to 3.0μ.

Specifically, it has been discovered that upon blending the aforementioned differentially sensitive silver halide dispersions, the characteristic curve of the dye transfer image resultant from employment of the blend assumes the "shoulder," i.e., low photosensitive silver halide layer photoexposure region, "speed," i.e., relative measurement defined as a value representing the reciprocal of the exposure required to produce a predetermined result, of the fastest silver halide dispersion and the "toe," i.e., high photosensitive layer photoexposure region, "speed" of the slowest silver halide dispersion, thus increasing the exposure latitude range and lowering the resutlant slope or gamma of the curve.

There is thus provided the capacity for controlled formulation of photosensitive layers exhibiting a selectively

extended range of predetermined gammas or contrasts and "exposure latitudes" or "dynamic ranges," i.e., the relative measurement of the range of exposure from which a useful dye transfer image may be derived; the instant invention thereby providing the capability of a high maximum density, low minimum density and extended dynamic range dye diffusion transfer imaging system and thus adapted to more advantageously reproduce, as dye transfer image differences, the luminance differences existing in an object to be photographically reproduced, including optimization of the minimum useful exposures required to reproduce minimum differences existing in the shadow regions of the object to be reproduced by means of some minimum density differences in resultant dye transfer image conformation.

Referring to FIGS. 8 and 9, there is set forth in each figure a graph showing the characteristic curves of a dye transfer image determined by plotting the reflection density of the transfer image as a function of the log exposure of the photosensitive silver halide layer wherein Curve A in FIG. 8 and D in FIG. 9 represent the characteristic curves of dye transfer images employing photosensitive silver halide emulsions comprising a silver halide dispersion >95% of which silver halide possesses a particle size of $1.3\mu \pm 10\%$; Curves D and E repersent the characteristic curves employing photosensitive silver halide emulsions comprising a silver halide dispersion >95% of which silver halide possesses a particle size of $0.9\mu \pm 10\%$ and wherein the photosensitive layers generating Curves A and D possess higher photographic speed or inherent sensitivity than those generating Curves B and E. Curves C and F denoted in FIGS. 8 and 9 represent the dye transfer image characteristic curves generated by 50:50 blends of the dispersions providing Curves A and B, and D and E, respectively.

Curves C and F in FIGS. 8 and 9 clearly exhibit the effect of blending the photosensitive silver halide dispersions generating Curves A and D with the less sensitive silver halide dispersions generating Curves B and E, and resultant Curves C and F illustrate that they are composites of Curves A and B, and D and E, respectively, possessing the shoulder speed of the more highly sensitive emulsion illustrated in Curves A and D and the toe speed of the less highly sensitive emulsion illustrated in Curves B and D and, with respect to Curve C, a composite gamma of 1.0 compound as compared with gammas of 2.9 and 2.7, respectively, for Curves A and B, and, with respect to Curve F, a composite gamma of 2.1 as compared with gammas of 2.9 and 2.7, respectively, for Curves D and E.

The results denoted illustrate graphically that desired dye transfer characteristic curve performance may be readily obtained by the blending of silver halide dispersions possessing required toe and shoulder speeds to provide selected composite sensitometric results.

For the production of the data denoted above, film units were prepared by coating a polyester film base, in order, with a layer of the cyan dye developer 1,4-bis-(β-[hydroquinonyl - α - methyl] - ethyl - amino) - 5,8-dihydroxy-anthraquinone dispersed in gelatin and coated at a coverage of ~70 mgs./ft.^{2} dye and ~70 mgs./ft.^{2} gelatin, a gelatino silver iodochlorobromide emulsion coated at a coverage of ~210 mgs./ft.^{2} silver and ~50 mgs./ft.^{2} gelatin, which has been prepared initially forming the predetermined narrow grain size emulsion, separating from the formulation undesired reaction products, and afterripening the resultant silver iodochlorobromide emulsion in combination with the selected auxiliary sensitizing, speed increasing, etc., adjuncts selected and, in the test structures, blending selected emulsion formulations.

Specifically, the emulsion may be readily formulated by a conventional double jet addition, over a period of one day, at a rate of 100 cc. per hour per jet, one jet delivering a solution comprising 3 M. silver nitrate, in distilled water, at room temperature, the second jet delivering a solution comprising a 3 M. alkali halide (e.g., potassium) possessing $95\% \pm 5\%$ bromide, $5\% \pm 5\%$ chloride, $2.5\% \pm 2.4\%$ iodide to equal 100%, in distilled water, at room temperature, to a 5% solution of gelatin in distilled water, at room temperature, preadjusted to pH 6 with 5% sodium hydroxide. The resultant silver iodochlorobromide emulsion is held subsequent to formulation for the period of time required to provide the selected silver halide grain size distribution and separated from the reaction mixture, i.e., the supernatant liquid and washed with chilled distilled water until the wash water exhibits a conductivity of ~300 to 500μ mhos./cm., the volume adjusted with distilled water for the addition of 20 gms. of gelatin per 1000 cc. of emulsion, and the emulsion then afterripening for 3 hours at a temperature of 60° C. and a pH of 5.5

A rupturable container, constructed as detailed hereinafter, containing an aqueous alkaline processing composition comprising:

	Percent
Potassium hydroxide	12.0
Hydroxyethyl cellulose	3.8
N-phenethyl-α-picolinium bromide	3.5
Benzotriazole	3.5
Potassium thiosulfate	0.5
4'-methylphenyl hydroquinone	0.4
Lithium nitrate	0.5

was then mounted on the leading edge of each film unit such that, subsequent to exposure of each unit and upon application of compressive force to a container, its contents are distributed, upon rupture of the contained distribution port, between the unit and the image-receptive layer of a contiguous dye transfer image-receiving element superposed coextensive the surface of the emulsion layer; the dye transfer image-receiving element prepared by coating, in order, with a polymeric acid layer comprising the partial butylester of polyethylene/maleic anhydride copolymer 0.7 mil. thick; a polymeric spacer layer comprising a 6:4 mixture, by weight of hydroxypropylcellulose and polyvinyl alcohol 0.3 mil. thick; and a polymeric image-receiving layer comprising a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4- vinyl pyridine 0.4 mil. thick and including about 20 mgs./ft.^{2} phenyl mercapto tetrazole.

It has been found that the advantages procured by means of the present invention are facilitated by maximizing restriction of the grain size distribution to the mean grain size selected to provide the results desired. Irrespective of such optimization, however, the photosensitivity response of the grains may be such as to provide a photoresponse gradient traditionally illustrated by the curve shape of the standard H & D type curve integrating processed silver image density as a function of film unit photoexposure.

It will be recognized that the employment of silver halide grain dispersions possessing maximally limited crystal size distribution and the last-mentioned photoresponse characteristics may be readily prepared in a plurality of expeditious manners, including the simple procedure which comprises the blending of dispersions possessing substantially homogeneous or uniform crystal size distribution wherein the silver halide crystal component of the dispersions forming the ultimate blend possesses differential electromagnetic radiation sensitivity.

The photoresponsive silver halide material employed in the practice of the present invention will, as previously described, comprises a crystal of a compound of silver, for example, one or more of the silver halides, such as photosensitive silver chloride, silver iodide, silver bromide, and preferably, mixed silver halides, such as silver chlorobromide, silver iodochloride, silver iodobromide or silver iodochlorobromide, of varying halides ratios and the silver concentrations dispersed in a processing composition permeable binder material such as gelatin and the like, most preferably silver iodobromide and

iodochlorobromide, particularly that comprising ~0.1 to 9% iodide by weight of silver.

In a particularly preferred embodiment of the present invention, >~75% and more preferably >~90% of the silver halide grains constituting the photosensitive layer possess a mean particle size within the stated range of ~0.5 to 3.0μ, and most preferably each silver halide dispersion constituting in intimate admixture the photosensitive layer possesses a substantially uniform grain size within the stated range, preferably within ±~10% of the selected grain size, i.e., ~0.5±10% of 3.0±10%μ.

The preferred silver halide type photosensitive layers employed for the fabrication of the photographic film unit, may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water soluble halide, such as ammonium, potassium or sodium chloride, preferably together with corresponding iodide and bromide in an aqueous solution of a peptizing agent such as colloidal gelatin solution; digesting the dispersion at an elevated temperature to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts for example, employing the preferred gelatin matrix material by chilling the dispersion, noodling the set dispersion and washing the noodles with cold water, or, alternatively, employing any of the various floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pats. Nos. 2,614,928; 2,614,929; 2,728,662, and the like; after ripening the dispersion at an elevated temperature in combination with the addition of gelatin or such other polymeric material as may be desired and various adjuncts, for exam the procedures described in U.S. Pats. No. 2,614,928; 2,614,929; 2,728,662, and the like; after ripening the dispersion at an elevated temperature in combination with the addition of gelatin or such other polymeric material as may be desired and various adjuncts, for example, chemical sensitizing agents of U.S. Pats. Nos. 1,574,-944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,-850; 2,518,698; 2,521,926; and the like all according to the traditional procedures of the art as described in Neblette, C. B., Photography Its Materials and Processes, 6th ed., 1962.

Optical sensitization of the emulsion's silver halide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the selected optical sensitizing dyes dissolved in an appropriate dispersing solvent such as methanol, ethanol, acetone, water, and the like; all according to the traditional procedures of the art, as described in Hammer, F. M., The Cyanine Dyes and Related Compounds.

Additional optional additives, such as coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, and the like, for example, those set forth hereinafter, also may be incorporated in the emulsion formulation, according to the conventional procedures known in the photographic emulsion manufacturing art.

As the binder for the photoresponsive material, the aforementioned gelatin may be, in whole or in part, replaced with some other natural and/or synthetic processing composition permeable polymeric material such as albumin; casein; or zein or resins such as cellulose derivative, as described in U.S. Pats Nos. 2,322,085 and 2,541,474; vinyl polymeric such as described in an extensive multiplicity of readily available U.S. and foreign patents or the photoresponsive material may be present substantially free of interstitial binding agent as described in U.S. Pats. Nos. 2,945,771; 3,145,566; 3,142,567; Newman, Comment on Non-Gelatin Film, B.J.O.P., 434, Sept. 15, 1961; and Belgian Pats. Nos. 642,557 and 642,558.

As previously mentioned, photosensitive silver halide emulsion dispersions possessing stated grain size distribution may be readily obtained by a plurality of conventional emulsion manufacturing procedures known to those skilled in the art, including procedures and apparatus particularly adapted to provide restricted and substantially homogeneous or uniform grain size distributions; see, for example, the processes and apparatus disclosed in U.S. Pats. Nos. 3,326,641 and 3,415,650, each of which is specifically hereby incorporated herein by reference.

A plurality of the procedures thus exist in the art, including those of the last-cited U.S. patents and applications, employ mechanical particle classifier apparatus and techniques adapted to differentially separate materials of varying densities and materials of the same density and varying mass, which are, accordingly, particularly adapted to classify silver halide grains into desired distribution ranges and, at the election of the operator, provide further concentration or dilution of emulsion fluid volume specifically including counter-current centrifugal exchange devices; conventional mechanical centrifugation devices and procedures; in process centrifugal force field extraction employing hydrocyclone devices and procedures, etc.; positive sedimentation devices and procedures; and the like.

In preferred embodiments of the present invention, the photosensitive silver halide dispersions employed will be emulsions adapted to provide in combination a Diffusion Transfer Process Exposure Index >~50, which Index indicates the correct exposure rating of a diffusion transfer color process at which an exposure meter, calibrated to the ASA Exposure Index, must be set in order that it give correct exposure data for producing color transfer prints of satisfactorily high quality. The Diffusion Transfer Process Exposure Index is based on a characteristic H & D curve relating original exposure of the photosensitive silver halide emulsions to the respective curve densities forming the resultant transfer image. Thus, the Diffusion Transfer Exposure Index is based on the exposure to which the photosensitive silver halide emulsions, for use in color diffusion transfer processes, must be subjected in order to obtain an acceptable color transfer image by that process and is a direct guide to the exposure setting to be entered in a camera in order to obtain proper exposure of the film unit.

In a preferred embodiment of the present invention, the means for interposing the processing composition selected intermediate the reception layer and the silver halide layer comprises a rupturable container retaining a processing composition comprising the solvent and pH concentrations required fixedly positioned and extending transverse a leading edge of the film unit to effect, upon application of compressive pressure, discharge of the processing composition intermediate the reception layer and the photosensitive silver halide layer next adjacent. In such embodiment the opacifying agent is preferably disposed within the processing composition, as retained in the rupturable container, for distribution as a component of such composition intermediate the reception and silver halide layers, subsequent to selective exposure of the film unit.

Multicolor images may be obtained using color image-forming components in the diffusion transfer process of the present invention by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing, for example, dye developers as dye image-providing materials by employment of an integral multilayer photosensitive element, such as is disclosed in my aforementioned U.S. Pat. No. 3,415,644 wherein at least two selectively sensitized photosensitive strata, superposed on a single support, are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises the opaque support carrying a red-sensitive silver halide stratum, a green-sensitive silver halide stratum and a blue-sensitive silver halide stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye de-

veloper may be utilized in the silver halide stratum, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide strata. Each set of silver halide strata and associated dye developer strata are disclosed to be optionally separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

In a preferred embodiment of the present invention, the film unit is specifically adapted to provide for the production of a mutlicolor dye transfer image and the photosensitive laminate comprises, in order of essential layers, the dimensionally stable opaque layer; at least two selectively sensitized silver halide strata each having dye image-providing material of predetermined color associated therewith, for example, dye developers as detailed above, which are soluble and diffusible in processing composition as a function of the point-to-point degree of exposure of the respective associated silver halide stratum; a polymeric layer dyeable by the dye image-providing materials; and a dimensionally stable transparent layer.

In view of the fact that the preferred dye image-providing materials comprise dyes which are silver halide developing agents, as stated above, for purposes of simplicity and clarity, the present invention will be further described hereinafter in terms of such dyes, without limitation of the invention to the illustrative dyes denoted, and, in addition the photographic film unit structure will be detailed hereinafter employing the last-mentioned preferred structural embodiment, without limitation of the invention to the preferred structure denoted.

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. The dye developers employed may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide stratum. Specifically, the dye developer may, for example, be in a coating or layer behind the respective silver halide stratum and such a layer of dye developer may be applied by use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer distributed in a film-forming natural, or synthetic, polymer, for example, gelatin polyvinyl alcohol, and the like, adapted to be permeated by the chosen diffusion transfer fluid processing composition.

The silver halide strata comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at a first pH possessing, subsequent to processing, a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion.

In the preferred embodiment, each of the silver halide strata, and its associated dye, is separated from the remaining strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers.

In such preferred embodiment of the invention, the silver halide strata comprises photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness; the dye itself is dispersed in an aqueous alkaline solution polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the dyeable polymeric layer is transparent and about 0.25 to 0.4 mil in thickness; and each of the dimensionally stable opaque and transparent layers are alkaline solution impermable, processing composition vapor permeable and about 2 to 6 mils in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

Although in point of fact, the dimensionally stable layers employed in the practice of the present invention may possess a vapor transmission rate of 1 or less gms./24 hrs./100 in.^{2}/mil., in a preferred embodiment of the present invention, the layers employed will possess a vapor transmission rate for the selected processing composition solvent averaging not less than about 100 gms./24 hrs./100 in.^{2}/mil., most preferably in terms of the preferred solvent, water, a vapor transmission rate averaging in excess of about 300 gms. of water/24 hrs./100 in.^{2}/mil., and may advantageously comprise a microporous polymeric film possessing a pore distribution which does not unduly interfere with the dimensional stability of the layers or, where required, the optical characteristics of such layers. Such pore distribution may comprise, for example, an average pore diameter of from $<\sim 20$ microns to $>\sim 100$ microns and a pore volume of $<\sim 3\%$ to $<\sim 7\%$.

In a particularly preferred embodiment of the present invention, the preferred solvent, water, may be employed in a weight/weight ratio of about 1:10 to 1:20 dye to water at a ratio of about 1:3 to 1:10 liquid permeable polymer to water and most preferably will be fabricated to comprise about 300 to 1300 mgs./ft.^{2} liquid permeable polymeric binder material, about 200 to 400 mgs./ft.^{2} dye and about 5000 mgs./ft.^{2} water.

The dimensionally stable layers are designed so that there is no liquid flow through the layers while allowing the vapor of the processing composition solvent to pass by diffusion from the evaporating liquid body and the operational efficiency of the film unit is directly dependent upon the nature and quality of the vapor permeable membrance characteristics of the layers selected. The vapor transmission characteristics desired are directed to maximization of the rate at which the required quantity of processing solvent is effectively evacuated from the film unit subsequent to substantial dye transfer image formation by diffusion transfer processing, commensurate with maintaining the liquid impermeability and dimensional stability characteristics of the layers. Thus, the layers should possess the maximum vapor transmission capacity which permits the passage of processing composition solvent vapor, and any gas dissolved therein, at its vapor pressure, without allowing passage of fluid processing composition. The layers employed in accordance with the present invention therefor should be as thin as possible for solvent vapor transmission efficiency yet retain sufficient strength to provide stability to and resist chemical and physical degradation of the film unit under conditions of use.

In the preferred embodiment of the present invention's film unit for the production of a multicolor transfer im-

age, the respective silver halide/dye developer units of the photosensitive element will be in the form of a tripack configuration which will ordinarily comprise a cyan dye developer/red-sensitive emulsion unit contiguous the dimensionally stable opaque layer, the yellow dye developer/blue-sensitive emulsion unit most distant from the opaque layer and the magenta dye developer/green-sensitive emulsion unit intermediate those units, recognizing that the relative order of such units may be varied in accordance with the desires of the operator.

Reference is now made to FIGS. 1 through 7 of the drawings wherein there is illustrated a preferred film unit of the present invention and wherein like numbers, appearing in the various figures, refer to like components.

As illustrated in the drawings, FIG. 1 sets forth a perspective view of the film unit, designated **10**, and each of FIGS. 2 through 7 illustrate diagrammatic cross-sectional view of film unit **10**, along the stated section lines **2—2**, **3—3**, **5—5** and **7—7**, during the various depicted stages in the performance of a photographic diffusion transfer process as detailed hereinafter.

Film unit **10** comprises rupturable container **11**, retaining, prior to processing, aqueous processing composition **12**, and photosensitive laminate **13**, including, in order, dimensionally stable opaque layer **14**, preferably an actinic radiation-opaque flexible sheet material; cyan dye developer layer **15**; red-sensitive silver halide emulsion layer **16**; interlayer **17**; magenta dye developer layer **18**; green-sensitive silver halide emulsion layer **19**; interlayer **20**; yellow dye developer layer **21**; blue-sensitive silver halide emulsion layer **22**; auxiliary layer **23**, which may contain an auxiliary silver halide developing agent; image-receiving layer **24**; spacer layer **25**; neutralizing layer **26**; and dimensionally stable transparent layer **27**, preferably an actinic radiation transmissive flexible sheet material.

The structural integrity of laminate **13** may be maintained, at least in part, by the adhesive capacity exhibited between the various layers comprising the laminate at their opposed surfaces. However, the adhesive capacity exhibited at an interface intermediate image-receiving layer **24** and the silver halide emulsion layer next adjacent thereto, for example, image-receiving layer **24** and auxiliary layer **23** as illustrated in FIGS. 2 through 7, should be less than that exhibited at the interface between the opposed surfaces of the remainder of the layers forming the laminate, in order to facilitate distribution of processing solution **12** intermediate the stated image-receiving layer **24** and the silver halide emulsion layer next adjacent thereto. The laminate's structural integrity may also be enhanced or provided, in whole or in part, by providing a binding member extending around, for example, the edges of laminate **13**, and maintaining the layers comprising the laminate intact, except at the interface between layers **23** and **24** during distribution of processing composition **12** intermediate those layers. As illustrated in the figures, the binding member may comprise a pressure-sensitive tape **28** securing and/or maintaining the layers of laminate **13** together at its respective edges. Tape **28** will also act to maintain processing solution **12** intermediate image-receiving layer **24** and the silver halide emulsion layer next adjacent thereto, upon application of compressive pressure to pod **11** and distribution of its contents intermediate the stated layers. Under such circumstances, binder tape **28** will act to prevent leakage of fluid processing composition from the film unit's laminate during and subsequent to photographic processing.

Rupturable container **11** may be of the type shown and described in any of U.S. Pats. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,492; 3,056,491; 3,152,515; and the like. In general, such containers will comprise a rectanguar blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls **29** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing composition **12** is retained. The longitudinal marginal seal **30** is made weaker than the end seals **31** so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **12** of the container by the application of compressive pressure to walls **29** of the container.

As illustrated in FIGS. 1, 2 and 3, container **11** is fixedly positioned and extends transverse a leading edge of photosensitive laminate **13** whereby to effect unidirectional discharge of the container's contents **12** between image-receiving layer **24** and the stated layer next adjacent thereto, upon application of compressive force to container **11**. Thus, container **11**, as illustrated in FIG. 2, is fixedly positioned and extends transverse a leading edge of laminate **13** with its longitudinal marginal seal **30** directed toward the interface between image-receiving layer **24** and auxiliary layer **23**. As shown in FIGS. 1, 2 and 4, container **11** is fixedly secured to laminate **13** by extension **32** of tape **28** extending over a portion of one wall **29** of the container, in combination with a separate retaining member such as illustrated retaining tape **33** extending over a portion of laminate **13**'s surface generally equal in area to about that covered by tape **28**.

As illustrated in FIGS. 1, 2 and 4, extension flap **32** of tape **28** is preferably of such area and dimensions that upon, for example, manual separation of container **11** and tape **33**, subsequent to distribution of processing composition **12**, from the remainder of film unit **10**, flap **32** may be folded over the edge of laminate **13**, previously covered by tape **33**, in order to facilitate maintenance of the laminate's structural integrity, for example, during the flexations inevitable in storage and use of the processed film unit, and to provide a suitable mask or frame, for viewing of the transfer image through the picture viewing area of transparent layer **27**.

The fluid contents of the container preferably comprise an aqueous alkaline solution having a pH and solvent concentration at which the dye developers are soluble and diffusable and contains inorganic light-reflecting pigment and at least one optical filter agent at a pH above the pKa of such agent in a quantity sufficient, upon distribution, effective to provide a layer exhibiting optical transmission density $>\sim 6.0$ and optical reflection density $<\sim 1.0$ to prevent exposure of photosensitive silver halide emulsion layers **16**, **19** and **22** by actinic radiation incident on dimensionally stable transparent layer **27** during processing in the presence of such radiation and to afford immediate viewing of dye image formation in image-receiving layer **24** during and subsequent to dye transfer image formation. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver halide emulsion or emulsions of laminate are appropriately protected by incident radiation, at one major surface of the opaque processing composition and at the remaining major surface by the dimensionally stable opaque layer. If the illustrated binder tapes are also opaque, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented.

The selected reflecting pigment should be one providing a background suitable for viewing the dye developer transfer image formed in the dyeable polymeric layer. In general, while susbtantially any reflecting agent may be employed, it is preferred that a reflecting agent be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, an agent which is aesthetically pleasing to the viewer and does not provide a background noise signal degrading, or detracting from, the information content of the image. Particularly desirable reflecting agents will be those providing a white background, for viewing the transfer image, and specifically those conventionally employed to provide background for reflection photographic prints and, especially those agents possessing the optical properties desired for reflection of incident radiation.

As examples of reflecting pigments adapted for employment in the practice of the present invention, mention may be made of barium sulfate, zinc sulfide, titanium, dioxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, and the like.

A particularly preferred reflecting agent comprises titanium dioxide due to its highly effective reflection properties. In general, in such preferred embodiment, based upon percent titanium dioxide (weight/volume) a processing composition containing about 1500 to 4000 mgs./ft.^{2} titanium dioxide dispersed in 100 cc. of water will provide a percent reflectance of about 85 to 90%. In the most preferred embodiments, the percent reflectance particularly desired will be in the order of $>\sim 85\%$.

In embodiments wherein the dispersion comprises a preformed layer positioned intermediate the reception layer and next adjacent silver halide layer, the pigment layer will be sufficiently transparent to allow transit of exposing radiation through the pigment layer and may comprise titanium dioxide reflecting agent possessing a particle size distribution averaging $<\sim 0.2$ microns in diameter and preferably $<\sim 0.05$ micron in diameter as initially present preceding exposure of the film unit, which preferred materials, upon contact with aqueous alkaline processing composition, preferably aggregate to provide particles possessing a diameter $>\sim 0.2$ micron in diameter and will be coated at a coverage of $\sim$200 to 1000 mgs./ft.^{2}. Specifically, the reflecting agent will be present in a quantity insufficient to prevent exposure of the emulsion layers by actinic radiation incident on the dimensionally stable transparent layer of the film unit but in a concentration sufficient, subsequent to processing, to mask dye developer associated with the silver halide emulsion strata from the dye transfer image. In the preferred construction of such embodiment, the pigment such as titanium dioxide will be initially present in a relatively small particle size to provide unexpectedly efficient transit of radiation through the reflecting layer during exposure which upon contact with an alkaline processing composition and aggregation of the pigment particles provides efficient light reflectivity and masking capacity subsequent to such aggregation.

In general, the reflecting agents to be employed are those which remain substantially immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible inorganic pigment dispersions within the layer in which they are disposed.

Where desired, reflecting agent pigment may thus be distributed in whole or in part within a processing composition permeable polymeric matrix such as gelatin and/or any other such polymeric matrixes as are specifically denoted throughout the specification as suitable for employment as a matrix binder and may be distributed in one or more of the film unit layers which may be separated or contiguous, intermediate the image-receiving layer and next adjacent silver halide layer, provided that its distribution and concentration is effective to provide the denoted post processing masking function, and/or in whole or in part the reflecting agent may be ultimately disposed within the processing composition residuum located intermediate the image-receiving layer and next adjacent silver halide emulsion strata and associated dye image-forming material.

The optical filter agent selected should be one exhibiting, at a pH above its pKa, maximum spectral absorption of radiation at the wavelengths to which the film unit's photosensitive silver halide layer or layers are sensitive and should be substantially immobile or nondiffusible within the pigment dispersion, during performance of its radiation filtration function, in order to maintain and enhance the optical integrity of the dispersion as a radiation filter unit functioning in accordance with the present invention, and to prevent its diffusion into and localized concentration within the image-receiving layer thereby decreasing the efficiency of the reflecting pigment dispersion as a background against which image formation may be immediately viewed, during the initial stages in the diffusion transfer processing of the film unit, by filter agent absorption of dispersion reflected visible radiation prior to reduction in the environmental pH below the pKa of the agent. Commensurate with the spectral sensitivity range of the associated silver halide layer or layers, the optical filter agent selected may comprise one or more filter dyes processing absorption complementary to such silver halide layers in order to provide effective protection against physical fog providing radiation during processing. Recognizing that the filter agent absorption will derogate from image-viewing characteristics by contaminating reflecting pigment background, the selected agents should be those exhibiting major spectral absorption at the pH at which processing is effected and minimal absorption at a pH below that which obtains during transfer image formation. Accordingly, the selected optical filter agent or agents should possess a pKa below that of the processing pH and above that of the environmental pH subsequent to transferimage formation, and will be preferably selected for employment in the minimum concentration necessary to provide an optical transmission density $>\sim 6.0$, at wavelengths at which the silver halide layer is maximally responsive, and an optical reflection density $<\sim 1.0$ at such wavelengths.

As specific examples of such pH-sensitive optical filter agents adapted for employment in the practice of the present invention, reference is directed to the agents set forth in aforementioned copending U.S. patent application Ser. No. 43,782, filed June 5, 1970, incorporated herein by reference.

In general, preferred agents, both opacifying and filter, are those which remain immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible materials.

As disclosed in the previously cited patents, the liquid processing composition referred to for effecting multicolor diffusion transfer processes comprises at least an aqueous solution of an alkaline material, for example, diethylamine, sodium hydroxide or sodium carbonate and the like, and preferably possessing a pH in excess of 12, and most preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms, a relatively firm and relatively stable film. The preferred film-forming materials disclosed comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Additionally, film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time are also disclosed to be capable of utilization. As stated, the film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 100 cps. at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature.

In the performance of a diffusion transfer multicolor process employing film unit **10**, the unit is exposed to radiation, actinic to photosensitive laminate **13**, incident on the laminate's exposure surface, as illustrated in FIG. 3.

Subsequent to exposure, as illustrated by FIGS. 2 and 4, film unit **10** is processed by being passed through opposed suitably gapped rolls **35** in order to apply compressive pressure to frangible container **11** and to effect rupture of longitudinal seal **30** and distribution of alkaline processing composition **12**, possessing inorganic light-

reflecting pigment and optical filter agent at a pH above the pKa of the filter agent and a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible as a function of the point-to-point degree of exposure of red-sensitive silver halide emulsion layer **16**, green-sensitive silver halide emulsion layer **19** and blue-sensitive silver halide emulsion layer **22**, respectively, intermediate reflecting agent precursor layer **25** and auxiliary layer **23**.

Alkaline processing composition **12** permeates emulsion layers **16**, **19** and **22** to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers **15**, **18** and **21**, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and non-diffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to dyeable polymeric layer **24** to provide a multicolor dye transfer image to that layer which is viewable against the background provided by the reflecting pigment present in processing composition residuum **12** masking cyan, magenta and yellow dye developer remaining associated with blue-sensitive emulsion layer **22**, green-sensitive emulsion layer **19** and red-sensitive emulsion layer **16**. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline processing composition **12** transfer, by diffusion, through permeable polymeric reception layer **24** permeable spacer layer **25** to polymeric neutralizing layer **26** whereby the environmental pH of the system decreases as a function of neutralization to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially nondiffusible to thereby provide a stable multicolor dye transfer image and discharge of the pH-sensitive optical filter agent by reduction of the pH substantially below the pKa of such agent to thereby provide maximum reflectivity in terms of the pigment concentration present.

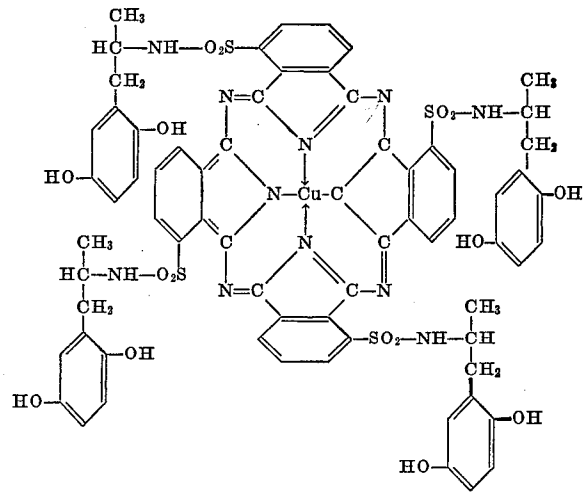
The alkaline solution component of the processing composition, positioned intermediate the photosensitive element and the image-receiving layer, thus permeates the emulsions to initiate development of the latent images contained therein. The respective associated dye developers are mobilized in unexposed areas as a consequence of the development of the latent images. This mobilization is apparently, at least in part, due to a change in the solubility characteristics of dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsions, the associated dye developer is diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image.

Subsequent to distribution of processing composition **12**, container **11** may be manually dissociated from the remainder of the film unit, as described above, to provide the product illustrated in FIG. 6.

The present invention will be further illustrated and detailed in conjunction with the following illustrative constructions which set out representative embodiments and photographic utilization of the novel photographic film units of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

Film units similar to that shown in the drawings may be prepared, for example, by coating, in succession, on a 5 mil. opaque polyester film base, the following layers:

(1) A layer of the cyan dye developer

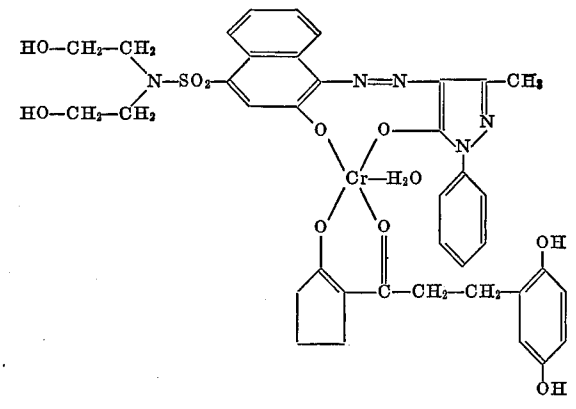


dispersed in gelatin and coated at a coverage of ~98 mgs./ft.^{2} of dye and ~92 mgs./ft.^{2} of gelatin;

(2) A red-sensitive gelatino-silver iodochlorobromide emulsion comprising a 6:4 blend of a silver halide dispersion >95% of a silver iodochlorobromide grains of which possess a diameter of 1.8 $\mu\pm10\%$ and a silver halide dispersion>95% of the silver iodochlorobromide grains of which possess a diameter of 1.0$\mu\pm10\%$, coated at a coverage of ~140 mgs./ft.^{2} of silver and ~27 mgs./ft.^{2} of gelatin;

(3) A layer of butyl acrylate/diacetone acrylamide/styrene/methacrylic acid (60/30/4/6) and polyacrylamide coated in a ratio of ~29:1, respectively, at a coverage of ~80 mgs./ft.^{2}.

(4) A layer of the magenta dye developer

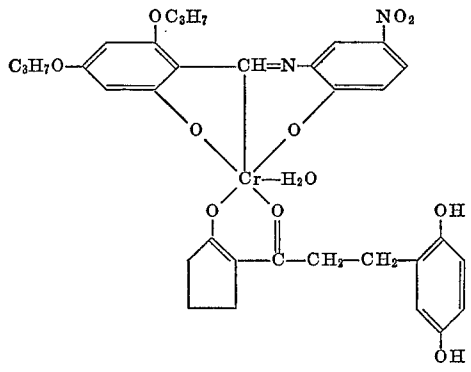


dispersed in gelatin and coated at a coverage of 71 mgs./ft.^{2} of dye and ~50 mgs./ft.^{2} of gelatin;

(5) A green-sensitive gelatino-silver iodochlorobromide emulsion comprising a 6:4 blend of a silver halide dispersion >95% of the silver iodochlorobromide grains of which possess a diameter of 1.3μ±10% and a silver halide dispersion >95% of the silver iodochlorobromide grains of which possess a diameter of 0.9μ±10%, coated at a coverage of ~80 mgs./ft.² of silver and 40 mgs./ft.² of gelatin;

(6) A layer comprising butyl acrylate/diacetone acrylamide/styrene/methacrylic acid (60/30/4/6) and polyacrylamide coated in a ratio of about 29:4, respectively, at a coverage of ~60 mgs./ft.²;

(7) A layer of the yellow dye developer



and the auxiliary developer 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of ~81 mgs./ft.² of dye, ~15 mgs./ft.² of auxiliary developer and 54 mgs./ft.² of gelatin;

(8) A blue-sensitive gelatino-silver iodochlorobromide emulsion comprising a 6:4 blend of a silver halide dispersion >95% of the silver iodochlorobromide grains of which possess a diameter of 1:1μ±10% and a silver halide dispersion >95% of the silver iodochlorobromide grains of which possess a diameter of 0.8μ±10%, coated at a coverage of ~65 mgs./ft.² of silver and ~33 mgs./ft.² of gelatin; and

(9) A layer of gelatin coated at a coverage of ~45 mgs./ft.² of gelatin.

Then a transparent 5 mil. polyester film base may be coated, in succession, with the following illustrative layers:

(1) A 7.3 mixture, by weight, of polyetheylene/maleic acid copolymer and polyvinyl alcohol at a coverage of about 1400 mgs./ft.², to provide a polymeric acid layer;

(2) A graft copolymer of acrylamide and diacetone acrylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 800 mgs./ft.², to provide a polymeric spacer layer; and

(3) A 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of about 900 mgs./ft.² and including about 20 mgs./ft.² phenyl mercapto tetrazole, to provide a polymeric image-receiving layer.

The two components thus prepared may then be taped together in laminate form, at their respective edges, by means of a pressure-sensitive binding tape extending around, in contact with, and over the edges of the resultant laminate.

A rupturable container comprising an outer layer of lead foil and an inner liner or layer of polyvinyl chloridie retaining an aqueous alkaline processing solution comprising:

	Gms.
Potassium hydroxide	11.20
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	3.40
N-Phenethyl-α-picolinium bromide	2.70
Benzotriazole	1.15
Titanium dioxide	50.00
Water, 100.00 cc.	

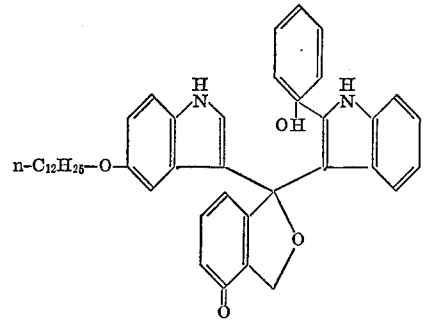
may then be fixedly mounted on the leading edge of each of the laminates, by pressure-sensitive tapes interconnecting the respective containers and laminates, such that, upon application of compressive pressure to a container, its contents may be distributed, upon rupture of the container's marginal seal, between the polymeric image-receiving layer and next adjacent gelatin layer.

The photosensitive composite film units may be exposed through radiation incident on the transparent cellulose triacetate layer and processed by passage of the exposed film units through appropriate pressure-applying members, such as suitably gapped, opposed rolls, to effect rupture of the container and distribution of its contents. Subsequent to processing, the multicolor dye transfer image formation may be viewed through the transparent polyester layer against the titanium dioxide background provided by distribution of the pigment containing processing composition between Layer 9 and the polymeric image-receiving layer. Multicolor dye transfer image formation will be found to be substantially completed and exhibiting the required color brilliance, hues, saturation and isolation, within a period of approximately 90 seconds.

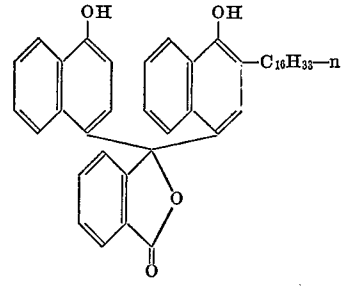
The gelatino silver iodochlorobromide emulsions employed will possess the silver halide distribution gradient detailed hereinbefore and may be prepared as previously detailed and chemically sensitized, at about 56° C., pH 5 and pAg 9, by the addition of a sensitizing amount of a solution containing 0.1 gram of ammonium thiocyanate in 9.9 cc. of water and 1.2 cc. of a solution containing 0.097 gram of gold chloride in 9.9 cc. of water, and a 0.02% aqueous sodium thiosulfate solution. The resultant emulsions may then be appropriately sensitized spectrally by addition of an effective concentration of one or more optical sensitizing dyes dispersed in an appropriate carrier solvent.

By addition of

(A) 2.08 gms.

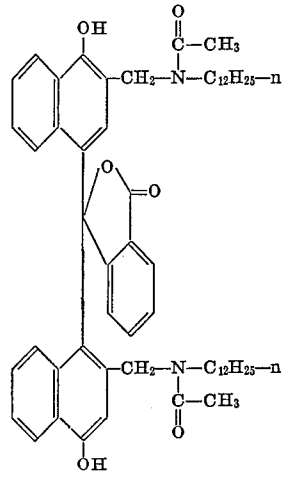


(B) 0.52 gms.



and

(C) 1.18 gms.



to the processing composition, image formation may be immediately viewed upon distribution of the processing composition by reason of the protection against incident radiation afforded the photosensitive silver halide emulsion layers by the composition's optical transmission density of $>\sim 6.0$ density units and against the titanium dioxide's effective reflective background afforded by reason of the composition possessing an optical reflection density $<\sim 1.0$ density units.

The pH and solvent concentration of the alkaline processing solution initially employed will possess a pH above the pKa of the optical filter agents where the latter are employed, that is, the pH at which about 50% of the agents are present as the lesser absorbing species and about 50% are present as the greater absorbing species, preferably a pKa of $>\sim 11$ and most preferably $>\sim 12$ and a pH at which the dye developers employed are soluble and diffusible. Although it has been found that the specific pH to be employed may be readily determined empirically for any dye developer and optical filter agent, or group of dye developers and filter agents, most particularly desirable dye developers are soluble at pH's above 9 and relatively insoluble at pH's below 9, in reduced form, and relatively insoluble at substantially any alkaline pH, in oxidized form, and the system can be readily balanced accordingly for such dye developers. In addition, although as previously noted, the processing composition, in the preferred embodiment, will include the stated film-forming viscosity-increasing agent, or agents, to facilitate spreading of the composition and to provide maintenance of the spread composition as a structurally stable layer of the laminate, subsequent to distribution, it is not necessary that such agent be employed as a component of the composition.

Neutralizing means, for example, a polymeric acid layer of the type discussed above may be incorporated, as stated, in the film unit of the present invention, to provide reduction of the alkalinity of the processing solution from a pH above the pKa of the optical filter agent selected at which the dyes are soluble to a pH below the pKa of the agent at which the dyes are substantially nondiffusible, in order to advantageously further stabilize and optimize reflectivity of the dye transfer image. In such instance, the neutralizing layer may comprise particulate acid reacting reagent disposed within the film unit or a polymeric acid layer, for example, a polymeric acid layer approximating 0.3 to 1.5 mils. in thickness, positioned intermediate the transparent support and image-receiving layer, and/or the opaque support and next adjacent emulsion/dye unit layer, and the film unit may also contain a polymeric spacer or barrier layer, for example, approximating 0.1 to 0.7 mil. in thickness, next adjacent the polymeric acid layer, opposite the respective support layer, as previously described.

Specifically, the film units may employ the presence of a polymeric acid layer such as, for example, of the type set forth in U.S. Pat. No. 3,362,819 which, most preferably, includes the presence of an inert timing or spacer layer intermediate the polymeric acid layer carried on a support and the image-receiving layer.

As set forth in the last-mentioned patent, the polymeric acid layer may comprise polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, retained in the polymer layer. In the preferred embodiments disclosed, the polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellu-lose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives or cellulose modified with sulfoanhydrides, e.g., with orthosulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether/maleic anhydride copolymers; etc.

As previously noted, the pH of the processing composition preferably is of the order of at least 12 to 14 and the pKa of the selected optical filter agents will accordingly preferably be in the order of 13 or greater. The polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition, thus requiring, of course, that the action of the polymeric acid be accurately so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer must be kept at a functional transfer level, for example, 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to a pH below that at which dye transfer may be accomplished, for example, at least about 11 and preferably about pH 9 to 10. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of, for example, 12 to 14 until transfer of the necessary quantity of dye has

been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the polymer layer may be effected by mixing acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only an acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthayl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also there disclosed that the layer containing the polymeric acid may contain a water-insoluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats are employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer of the last-mentioned patent, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It is there stated to have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As disclosed in aforementioned U.S. Pat. No. 3,362,819, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when imbibition is effected at temperatures above room temperature, for example, at 95 to 100° F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rates.

However, as disclosed in U.S. Pat. No. 3,455,686 preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended range of ambient temperatures.

Specifically, it is there stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true to alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective with the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last-mentioned inert spacer layer was disclosed to provide an effective diffusion barrier timewise preventing effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates and to result in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its resultant degradation of the positive transfer images' color definition.

It is further stated in the last-mentioned U.S. Pat. No. 3,455,686 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

As examples of polymers which were disclosed to exhibit inverse temperature-dependent permeability to alkali, mention may be made of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidone, hydroxypropyl methyl cellulose, isopropyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like.

The last-mentioned specified acetals of polyvinyl were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1000, preferably of about 1000 to 50,000, possessing a degree of acetalation within about 10 to 30%, 10 to 30%, 20 to 80%, and 10 to 40%, of the polyvinyl alcohol's theoretical polymeric hydroxy groups, respectively, and including mixed acetals where desired.

Where desired, a mixture of the polymers may be employed, for example, a mixture of hydroxypropyl methyl cellulose and partial polyvinyl butyral.

Employment of the detailed and preferred film units of the present invention, according to the herein described color diffusion transfer process, specifically provides for the production of a highly stable transfer image accomplished, at least in part, by effectively obviating the previously discussed disadvantages of the prior art products and processes, by in process adjustment of the environmental processing composition solvent and pH concentration from a solvent and pH concentration at which dye diffusion or transfer is operative to a solvent and pH concentration at which dye transfer is inoperative subsequent to substantial transfer image formation. The stable color transfer image is obtained irrespective of the fact that the film unit is maintained as an integral laminate unit during exposure, processing, viewing, and storage of the unit. Accordingly, by means of the present invention, multi-color transfer images may be provided over an extended processing temperature range which exhibit desired maximum and minimum dye transfer image densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation. These unexpected advantages are in addition to the manufacturing advantages obtained by reason of the present invention's integral color transfer film unit construction and which will be readily apparent from examination of the unit's parameters, that is, for example, advantages in more efficient utilization of fabricating materials and components, enhanced simplicity of film manufacture and camera design and construction, and more simplified and effectively controlled customer utilization of the unit.

The dimensionally stable support layers referred to may comprise any of the various types of conventional opaque and transparent rigid or flexible materials possessing the requisite liquid impermeability and vapor transmissivity denoted above, and may comprise polymeric films of both synthetic types and those derived from naturally occurring products. Particularly suitable materials include aqueous alkaline solution impermeable, water vapor permeable, flexible polymeric materials such as vapor permeable polymeric films derived from ethylene glycol terephthalic acid, vinyl chloride polymers; polyvinyl acetate; polyamides; polymethacrylic acid methyl and ethyl esters; cellulose derivatives such as cellulose, acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate; alkaline solution impermable, water vapor permeable papers; crosslinked polyvinyl alcohol; regenerated cellulose; and the like.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylon as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964.

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenyl, 2,4-diaminophenol, p-benzylaminophenyl, hydroquinone, toluhydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Pat. No. 3,039,869, issued June 19, 1962. As examples of suitable combinations of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethyleneimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in any one or more of the silver halide emulsion strata, the strata containing the dye developers, the interlayers, the overcoat layer, the image-receiving layer, or in any other auxiliary layer, or layers, of the film unit. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposure silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed in U.S. Pat. No. 3,173,786, issued Mar. 16, 1965.

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, etc., other than those specifically mentioned, provided that the pH of the composition is initially at the first pH and solvent concentration required. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

In all examples of this specification, percentages of components are given by weight unless otherwise indicated.

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of additional U.S. patents detailing specific dye developers for photographic transfer process use, mention may also be made of U.S. Pats. Nos. 2,983,605; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

As additional examples of synthetic, film-forming, permeable polymers particularly adapted to retain dispersed dye developer, mention may be made of nitrocarboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl-α,β-unsaturated carboxamides and copolymers of N-alkyl-α,β-carboxamides with N-hydroxyalkyl-α,β-unsaturated carboxamides, as disclosed in U.S. Pat. No. 3,069,263; copolymers of vinylphthalimide and α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxylic acids and terpolymers of N-vinylpyrrolidones, α,β-unsaturated carboxylic acids and alkyl esters of α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,044,873; copolymers of N,N-dialkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers of N-aryl- and N-cycloalkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,069,296; and the like.

In addition to conventional techniques for the direct dispersion of a particulate solid material in a polymeric, or colloidal, matrix such as ball-milling and the like techniques, the preparation of the dye developer dispersion may also be obtained by dissolving the dye in an appropriate solvent, or mixture of solvents, and the resultant solution distributed in the polymeric binder, with optional subsequent removal of the solvent, or solvents, employed, as, for example, by vaporization where the selected solvent, or solvents, possesses a sufficiently low boiling point or washing where the selected solvent, or solvents, possesses a sufficiently high differential solubility in the wash medium, for example, water, when measured against the solubility of the remaining composition components, and/or obtained by dissolving both the polymeric binder and dye in a common solvent.

For further detailed treatment of solvent distribution systems of the types referred to above, and for an extensive compilation of the conventional solvents traditionally employed in the art to effect distribution of photographic color-providing materials in polymeric binders, specifically for the formation component layers of photographic film units, reference may be made to U.S. Pats. Nos. 2,269,158; 2,322,027; 2,304,939; 2,304,940; 2,801,171; and the like.

Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,-

551; 3,227,552; 3,227,554; 3,243,294; 3,330,655; 3,347,-671; 3,352,672; 3,364,022; 3,443,939; 3,443,940; 3,443,-941; 3,443,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. No. 2,774,668 and 3,087,817, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, an appropriate dye developer in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will comprise minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan, a magenta and a yellow dye developer.

The present invention also includes the employment of a black dye developer and the use of a mixture of dye developers adapted to provide a black-and-white transfer image, for example, the employment of dye developers of the three subtractive colors in an appropriate mixture in which the quantities of the dye developers are proportioned such that the colors combine to provide black.

Where in the specification, the expression "positive image" has been used, this expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive emulsion layers. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive emulsion layers will be a positive and the dye image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

It will be recognized that, by reason of the preferred film unit's structural parameters, the transfer image formed upon directed exposure of the film unit to a selected subject and processing, will be a geometrically reversed image of the subject. Accordingly, to provide transfer image formation geometrically nonreversed, exposure of such film unit should be accomplished through an image reversing optical system such a camera possessing an image reversing optical system.

In addition to the described essential layers, it will be recognized that the film unit may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as platicizers, intermediate essential layers for the purpose, for example, of improving adhesion, and that any one or more of the described layers may comprise a composite of two or more strata of the same, or different components and which may be contiguous, or separated from, each other, for example, two or more neutralizing layers or the like, one of which may be disposed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable opaque layer.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic diffusion transfer color process film unit which comprises a plurality of layers including a direct negative photosensitive layer having associated therewith dye image-forming material which is diffusible during processing of the unit as a function of the point-to-point degree of said photosensitive layer's exposure to incident actinic radiation and comprising a plurality of photosensitive silver halide dispersions each comprising silver halide grains the majority of which possess a substantially uniform grain size, said dispersions taken together possessing a mean silver halide grain particle size within the range of $\sim$0.5 to 3.0μ, and a layer adapted to receive dye image-forming material diffusing thereto.

2. A photographic diffusion transfer color process film unit as defined in claim **1** wherein $>\sim$75% of said photosensitive silver halide grains constituting each said dispersion possess a substantially uniform grain size within the range of $\sim$0.5 to 3.0μ.

3. A photographic diffusion transfer color process film unit as defined in claim **2** wherein $>\sim$90% of said photosensitive silver halide grains constituting each said dispersion possess a substantially uniform grain size within the range of $\sim$0.5 to 3.0μ.

4. A photographic diffusion transfer color process film unit as defined in claim **1** wherein said substantially uniform photosensitive silver halide grains are within $\pm\sim$10% of the selected grain size.

5. A photographic diffusion transfer color process film unit as defined in claim **1** wherein at least two of said photosensitive silver halide dispersions possess different silver halide grain mean particle sizes.

6. A photographic diffusion transfer color process film unit as defined in claim **5** including opacifying agent, in a quantity sufficient to mask dye image-forming material associated with said photosensitive silver halide layer, adapted to be disposed intermediate said photosensitive silver halide layer and said layer adapted to receive dye image-forming material diffusing thereto.

7. A photographic diffusion transfer color process film unit as defined in claim **5** including means for contacting said photosensitive silver halide layer with a processing composition possessing a pH at which said dye image-forming material is soluble and diffusible as a function of the point-to-point degree of said photosensitive silver halide layer's exposure to incident actinic radiation.

8. A photographic diffusion transfer color process film unit as defined in claim **7** including means for converting the pH of said processing composition from said pH at which said dye image-forming material is soluble and diffusible as a function of said photosensitive silver halide layer's exposure to incident actinic radiation to a second pH at which said dye image-forming material is substantially nondiffusible, subsequent to substantial diffusion of solubilized dye image-forming material to said layer adapted to receive said dye image-forming material diffusing thereto.

9. A photographic diffusion transfer color process film unit as defined in claim **7** wherein said means for contacting said photosensitive silver halide layer with said proc-

essing composition comprises a rupturable container retaining said processing composition positioned extending transverse an edge of the film unit to effect, upon application of compressive pressure to said container, discharge of said container's processing composition contents into contact with said photosensitive silver halide layer.

10. A photographic diffusion transfer color process film unit as defined in claim **9** wherein said rupturable container retaining said processing composition is adapted, upon application of compressive pressure to the container, to discharge the container's processing composition contents intermediate said photosensitive silver halide layer and the layer adapted to receive dye image-forming material diffusing thereto.

11. A photographic diffusion transfer color process film unit as defined in claim **10** wherein said processing composition includes opacifying agent in a quantity sufficient to mask dye image-forming material associated with said photosensitive silver halide layer.

12. A photographic diffusion transfer color process film unit as defined in claim **11** including a dimensionally stable opaque layer positioned contiguous the surface of said photosensitive silver halide layer opposite said layer adapted to receive dye image-forming material diffusing thereto.

13. A photographic diffusion transfer color process film unit as defined in claim **12** including a dimensionally stable transparent layer positioned contiguous the surface of said layer adapted to receive dye image-forming material diffusing thereto opposite said photosensitive silver halide layer.

14. A photographic diffusion transfer color process film unit as defined in claim **1** wherein said dye image-forming material is a dye which is a silver halide developing agent.

15. A photographic diffusion transfer color process film unit as defined in claim **1** including a dimensionally stable layer positioned contiguous the surface of said photosensitive silver halide layer opposite said layer adapted to receive dye image-forming material diffusing thereto and additionally including at least two selectively sensitized silver halide layers comprising a plurality of photosensitive silver halide dispersions in intimate admixture, said dispersions comprising silver halide grains the majority of which possess a substantially uniform grain size distribution within the range of ~0.5 to 3.0μ and having a dye image-forming material associated therewith.

16. A photographic diffusion transfer color process film unit as defined in claim **15** wherein each of the selectively sensitized silver halide layers possesses predominant spectral sensitivity to separate regions of the spectrum and the dye image-forming material associated with each of said silver halide layers possesses a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated silver halide layer.

17. A photographic diffusion transfer color process film unit as defined in claim **16** wherein each of said selectively sensitized silver halide layers comprises a plurality of photosensitive silver halide dispersions in intimate admixture, said dispersions comprising photosensitive silver halide grains, >~75% of which are within ±~10% of the selected grain size within said range of ~0.5 to 3.0μ.

18. A photographic diffusion transfer color process film unit as defined in claim **17** which comprises, in combination:

a photosensitive element including a composite structure containing, as essential layers, a dimensionally stable opaque layer; at least two selectively sensitized silver halide emulsion layers possessing predominant spectral sensitivity to separate regions of the visible electromagnetic spectrum, said silver halide emulsion layers comprising photosensitive silver halide grains wherein >~90% of said grains possess a uniform grain size distribution within the range of ~0.5 to 3.0μ ±~10% of the selected grain size and said emulsion layers have associated therewith a dye which is a silver halide developing agent and is soluble and diffusible, in alkaline processing composition, at a first pH, possessing a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated emulsion layer; an alkaline solution permeable and dyeable polymeric layer; a polymeric layer possessing acid capacity effective, subsequent to substantial dye transfer image formation in said dyeable polymeric layer, to reduce alkaline processing composition possessing said first pH at which said dyes are soluble and diffusible to a second pH at which said dyes are substantially nondiffusible; a dimensionally stable transparent layer; and means securing the layers in substantially fixed relationship; and

a rupturable container retaining an alkaline processing composition possessing said first pH at which said dyes are soluble and diffusible and opacifying agent in a quantity sufficient to mask dye associated with said selectively sensitized silver halide emulsion layers, said rupturable container positioned and extending transverse an edge of the photosensitive element to effect unidirectional discharge of the container's alkaline processing composition intermediate the dyeable polymeric layer and the selectively sensitized silver halide emulsion layer next adjacent thereto.

19. A photographic diffusion transfer color process film unit as defined in claim **18** adapted to be processed by passage of said unit between a pair of juxtaposed pressure-applying members and which comprises, in combination:

a photosensitive element including a composite structure containing, as essential layers, in sequence, a dimensionally stable alkaline solution impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye, each of said red-, green- and blue-sensitive silver halide emulsion layers comprising a plurality of photosensitive silver halide dispersions in intimate admixture, said dispersions comprising silver halide grains, 90% of which possess a uniform grain size distribution within the range of ~0.5 to 3.0μ ±~10% of the selected grain size and said cyan, magenta and yellow dyes are silver halide developing agents soluble and diffusible, in alkaline processing composition, at a first pH; an alkaline solution permeable and dyeable polymeric layer; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition having said first pH at which said cyan, magenta and yellow dyes are soluble and diffusible to a second pH at which said cyan, magenta and yellow dyes are substantially nondiffusible; a dimensionally stable alkaline solution impermeable transparent layer; and means securing said layers substantially in fixed relationship; and

a rupturable container retaining an aqueous alkaline processing composition having said first pH at which cyan, magenta and yellow dyes are soluble and diffusible and opacifying agent in a quantity sufficient to mask, upon distribution of the aqueous alkaline processing composition as a layer, intermediate the dyeable polymeric layer and said blue-sensitive silver halide emulsion layer, cyan, magenta and yellow dye associated with said red-, green-, and blue-sensitive emulsion layers, said container fixedly positioned and extending transverse an edge of the photosensitive element to effect, upon application of compressive force to said container, unidirectional discharge of the container's aqueous alkaline proc-

essing composition contents intermediate said dyeable polymeric layer and said blue-sensitive silver halide emulsion layer.

20. A process of forming transfer images in color which comprises, in combination, the steps of:

(a) exposing a photographic film unit which includes, in combination, a photosensitive element containing a direct negative photosensitive silver halide layer having associated therewith dye image-providing material which is diffusible during processing as a function of the point-to-point degree of the photosensitive layer's exposure to incident actinic radiation and comprising a plurality of photosensitive silver halide dispersions each comprising silver halide grains the majority of which possess a substantially uniform grain size, said dispersions taken together possessing a mean silver halide grain particle size within the range of ~0.5 to 3.0μ;

(b) contacting said photosensitive silver halide emulsion with a processing composition;

(c) effecting thereby development of said photoexposed silver halide layer;

(d) forming thereby an imagewise distribution of diffusible dye image-providing material, as a function of the point-to-point degree of said silver halide layer's exposure to incident actinic radiation; and

(e) transferring by diffusion at least a portion of said imagewise distribution of said diffusible dye image-providing material to an image-receiving element dyeable by said dye image-providing material to provide thereto a dye image in terms of said imagewise distribution.

21. A process of forming transfer images in color as defined in claim **20** wherein >~75% of said photosensitive silver halide grains constituting said dispersions possess a substantially uniform grain size distribution within the range of ~0.5 to 3.0μ.

22. A process of forming transfer images in color as defined in claim **21** wherein >~90% of said photosensitive silver halide grains constituting said dispersions possess said substantially uniform grain size distribution within the range of ~0.5 to 3.0μ.

23. A process of forming transfer images in color as defined in claim **20** wherein said substantially uniform photosensitive silver halide grains constituting each dispersion are within ±~10% of the selected grain size of each said dispersion.

24. A process of forming transfer images in color as defined in claim **20** wherein said dye image-providing material is a dye which is a silver halide developing agent.

25. A process of forming transfer images in color as defined in claim **20** wherein said photosensitive element comprises in contiguous relationship at least two selectively sensitized silver halide layers having associated therewith a dye image-providing material which is diffusible during processing as a function of the point-to-point degree of the photoexposure of its associated silver halide layer, said silver halide layers comprising a plurality of photosensitive silver halide dispersions wherein >~75% of the silver halide grains constituting each dispersion possesses a selected grain size ±~10% within the range of ~0.5 to 3.0μ.

26. A process of forming transfer images in color as defined in claim **25** wherein said selectively sensitized silver halide layers possess predominant spectral sensitivity to separate regions of the visible spectrum and the dye image-providing material associated with each of said emulsion layers provides a dye possessing subsequent to processing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion layer.

27. A process of forming transfer images in color as defined in claim **26** wherein each of said silver halide layers and its associated dye is separated from the next adjacent layer and its associated dye by an alkaline solution permeable polymeric interlayer.

28. A process of forming transfer images in color as defined in claim **26** wherein said photosensitive element contains, as essential layers, in sequence, a support layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye, each of said cyan, magenta and yellow dyes being a silver halide developing agent and each of said red-, green- and blue-sensitive silver halide emulsion layers comprising a plurality of photosensitive silver halide dispersions wherein >~90% of the silver halide grains of each dispersion possesses a grain size distribution within the range of ~0.5 to 3.0μ±~10% of a selected grain size, and wherein said image-receiving element contains, as essential layers, in sequence, an alkaline solution permeable polymeric layer dyeable by said dyes; and a support layer.

29. A process of forming transfer images in color as defined in claim **28** wherein said film unit includes means for converting the pH of said processing composition from a first processing pH at which said cyan, magenta and yellow dyes are diffusible to a second pH at which said dyes are substantially nondiffusible and including the step of converting said film unit from said first pH to said second pH subsequent to substantial imagewise transfer of dye from said photosensitive element to said image-receiving element.

References Cited

UNITED STATES PATENTS

3,501,305	3/1970	Illingsworth	96—108
3,415,644	12/1968	Land	96—3

NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—76 C, 77